

Basis set convergence in extended systems: infinite hydrogen fluoride and hydrogen chloride chains

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Abstract

Basis set convergence of the Hartree-Fock and the correlation energy is examined for the hydrogen bonded *infinite* bent chains $(\text{HF})_\infty$ and $(\text{HCl})_\infty$. We employ series of correlation consistent basis sets up to quintuple ζ quality together with a coupled cluster method (CCSD) to describe electron correlation on *ab initio* level. The Hartree-Fock energy converges rapidly with increasing basis set quality whereas the correlation energy is found to be slowly convergent for the same series of basis sets. We study basis set extrapolation for $(\text{HF})_\infty$ and $(\text{HCl})_\infty$ and show that it substantially enhances the accuracy of both the Hartree-Fock and the correlation energy in *extended* systems.

Key words: electron correlation, ab initio calculations, hydrogen fluoride, hydrogen chloride, infinite bent chains, basis set convergence, basis set extrapolation

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1 Introduction

Ab initio methods for polymers and crystals come more and more into focus of quantum chemists and solid state physicists [1, 2]. As most *ab initio* treatments of such extended systems rely on incomplete one-particle basis sets, we consider it timely to investigate the basis set convergence of Hartree-Fock and correlation energies in *periodic* systems. *Molecular* Hartree-Fock energies are well known to converge exponentially, e.g. Ref. [3], towards the basis set limit,

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but molecular correlation energies turn out to converge only with the third power of the highest angular momentum employed in the basis sets [4, 5].

The convergence properties of the Hartree-Fock and the correlation energy can be exploited to extrapolate Hartree-Fock [3] and correlation energies [5–10] towards the basis set limit. As only standard methods of quantum chemistry are required, basis set extrapolation of correlation energies provides an interesting alternative over the specialised, explicitly correlated (R12) methods, which directly yield near basis set limit wave functions and correlation energies but have a high computational demand [5]. Especially well suited in conjunction with extrapolation schemes, are the correlation consistent basis sets [11] cc-pVXZ [12, 13], aug-cc-pVXZ [12–14] and d-aug-cc-pVXZ [12, 14, 15], $X = D, T, Q, 5, 6$ which are hierarchical series of basis sets of increasing quality.

Our study elucidates the performance of basis set extrapolation for Hartree-Fock and correlation energies in *infinite* periodic systems, the hydrogen bonded bent chains $(HF)_\infty$ and $(HCl)_\infty$ which are representatives for strong and weak hydrogen bonds [16] and require a very accurate description by a large one particle basis to reliably determine their binding energies per monomer. Hartree-Fock energies of the infinite chains are obtained by periodic calculations [17] whereas their correlation energy is calculated utilising Stoll’s incremental scheme [18–20] which has been successfully applied to various semiconductors [21, 22], ionic crystals [23, 24], rare gas crystals [25] and polymers [26–28].

2 Theory

Hartree-Fock energies turn out to converge rapidly with increasing basis set quality towards the basis set limit. However, the actual convergence behaviour has only empirically been determined, Ref. [3] (and Refs. therein), to depend both on the number of basis functions and on the highest angular momentum in basis sets. The cardinal number X of correlation consistent basis sets is related to both quantities, and Hartree-Fock energies follow

$$E_{\text{SCF}}(\infty) = E_{\text{SCF}}(X) - A e^{-BX} , \quad (1)$$

with $A, B > 0$ and $E_{\text{SCF}}(\infty)$ being the Hartree-Fock basis set limit while the Hartree-Fock energy obtained with a basis set X is denoted by $E_{\text{SCF}}(X)$.

Correlation energies converge differently; the partial wave analysis of the correlation energy of the helium atom [4] facilitates to derive the relation [6, 7]

$$E_{\text{corr}}(\infty) = E_{\text{corr}}(X) - A' X^{-3} , \quad (2)$$

where $E_{\text{corr}}(\infty)$ is the basis set limit correlation energy and $E_{\text{corr}}(X)$ represents the correlation energy obtained with basis set X (in our case, X is equal to the highest angular momentum of basis functions in the basis set).

Eq. (2) is derived for the asymptotic behaviour, i.e. large X , of the correlation energy, assuming basis sets of highest angular momentum X , being centred around a single point in space. The basis sets are supposed to be complete for all angular momenta $\leq X$ and are required to be complete with respect to their radial part [4]. However, a simple two-point fit based on Eq. (2), which involves the correlation energies of two basis sets X and Y , turns out to yield highly accurate molecular binding energies [6–8].

The extrapolation scheme for correlation energies of Park, Huh and Lee [9,10] is a more flexible basis set extrapolation which we consider to cope slightly better with the increasing radial and angular completeness of hierarchical basis set series. Park et al. harness

$$E_{\text{corr}}^{\text{chain}}(\infty) = \frac{E_{\text{corr}}^{\text{chain}}(X) - \gamma_{X,Y} E_{\text{corr}}^{\text{chain}}(Y)}{1 - \gamma_{X,Y}} \quad (3a)$$

$$\gamma_{X,Y} = \frac{E_{\text{corr}}^{\text{monomer}}(X) - E_{\text{corr}}^{\text{monomer}}(\infty)}{E_{\text{corr}}^{\text{monomer}}(Y) - E_{\text{corr}}^{\text{monomer}}(\infty)}, \quad (3b)$$

with the underlying assumption that the basis set convergence rate $\gamma_{X,Y}$ is the same for a monomer and an infinite chain formed by many monomers. $\gamma_{X,Y}$ is the ratio of the absolute error in the correlation energy of the monomer described by two different basis sets X and Y . If the electronic structure of a monomer does not change substantially upon chain formation, a given basis set represents both the monomer and the infinite chain equally well.

3 Results and discussion

Basis set extrapolation of Hartree-Fock and correlation energies shall now be used to obtain accurate binding energies of $(\text{HF})_{\infty}$ and $(\text{HCl})_{\infty}$ chains. Both $(\text{HF})_{\infty}$ and $(\text{HCl})_{\infty}$ form zig-zag chains where in both cases the unit cell consists of two monomers. Details concerning the employed experimental geometries can be found in Refs. [16, 29, 30].

The Hartree-Fock binding energies per monomer¹ are plotted for $(\text{HF})_{\infty}$ and $(\text{HCl})_{\infty}$ in Figs. 1 and 2. The basis set superposition error (BSSE) is removed beyond microhartree accuracy by counterpoise correction (CP) [31,32], where

¹ The Hartree-Fock energies of the infinite chains and the corresponding monomers were determined with CRYSTAL [17] where angular momenta, larger than s , p , d had to be removed from the basis sets.

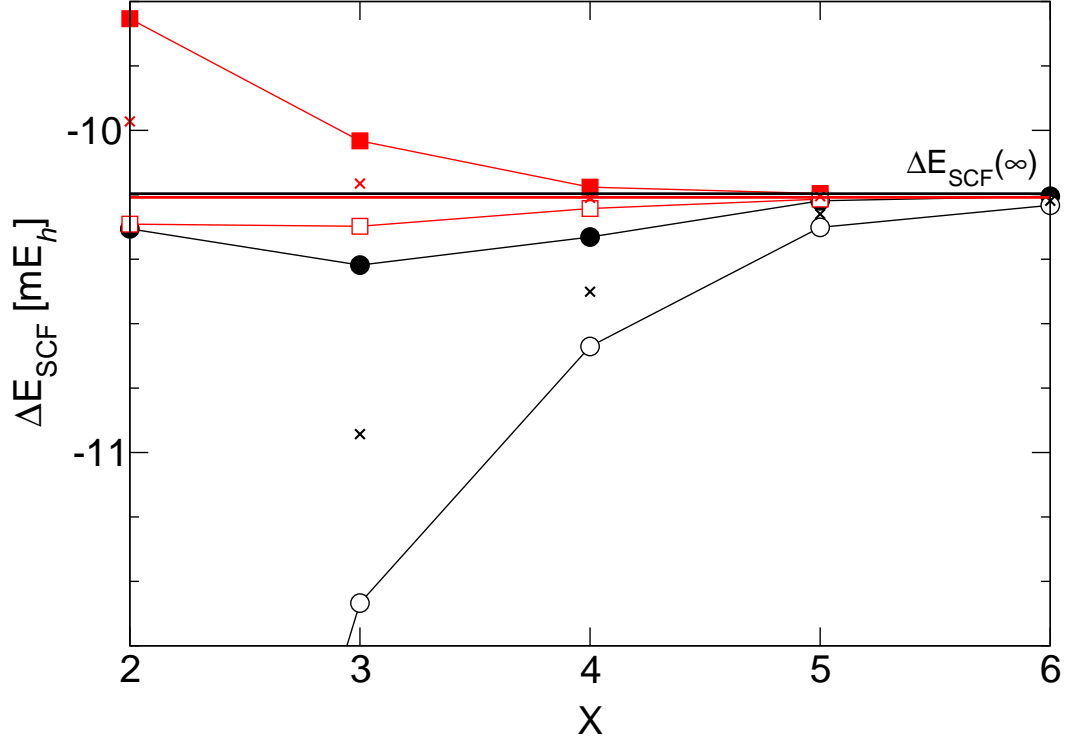


Fig. 1. Basis set convergence of the Hartree-Fock binding energy per monomer ΔE_{SCF} in $(\text{HF})_{\infty}$. Circles and squares represent $\Delta E_{\text{SCF}}(X)$ of the cc-pVXZ and aug-cc-pVXZ basis sets where open and closed symbols denote bare and CP corrected Hartree-Fock binding energies. The straight line results from two nearly coinciding lines which indicate the extrapolated Hartree-Fock binding energies, the upper and the lower line referring to the cc-pVXZ and the aug-cc-pVXZ basis sets. The crosses indicate the mean of the CP corrected and the corresponding bare Hartree-Fock binding energies.

a monomer is additionally surrounded by the basis functions of eight neighbouring monomers. For each series of correlation consistent basis sets, there is an upper curve for the CP corrected binding energies and a corresponding lower curve giving the bare binding energies without CP correction of the monomer energies. Both curves converge unsystematically towards the Hartree-Fock basis set limit, especially, they generally converge not monotonic.

The deviation of the lower curve from the upper curve of the same basis set series yields an estimate of the error of the approximation introduced by the finite basis sets as this deviation is the size of the BSSE [32] and an estimate of the incompleteness of a one-particle basis set. It is very small, 0.27% for $(\text{HF})_{\infty}$ and 2.7% for $(\text{HCl})_{\infty}$, utilising cc-pV6Z basis sets. Nevertheless, we would like to elucidate whether, in case of an infinite chain, the Hartree-Fock energies follow Eq. (1) as well, i.e. whether the packing in infinite periodic systems has an unexpected impact on Hartree-Fock basis set convergence. Tab. 1 gives Hartree-Fock energies at the basis set limit for the monomers and the infinite

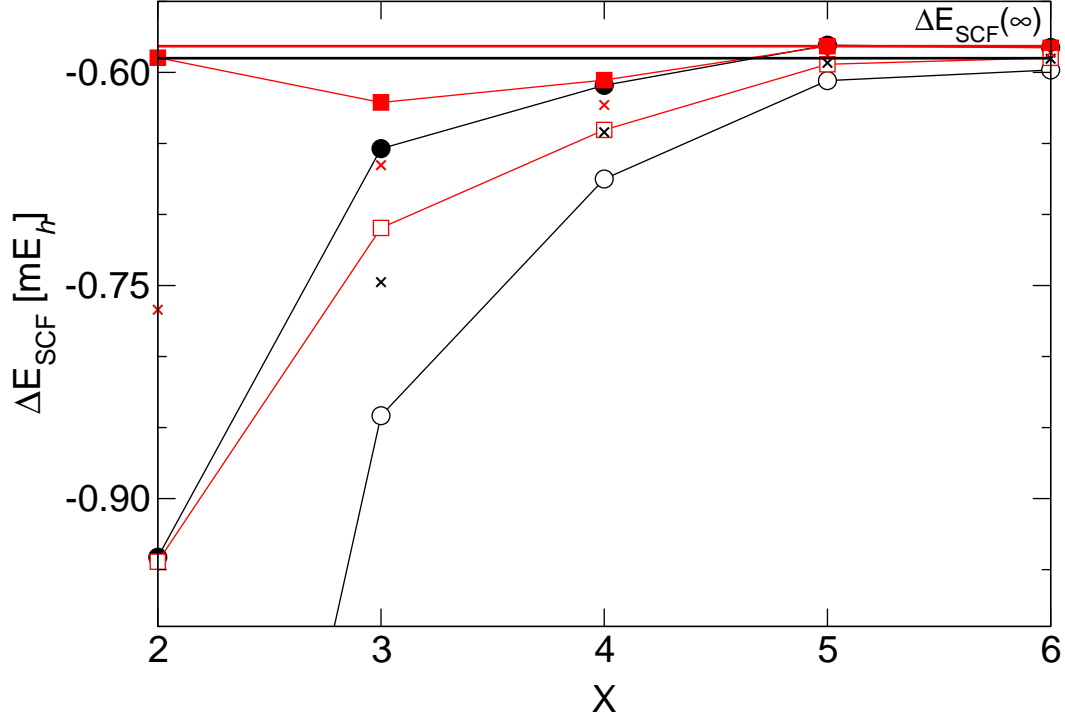


Fig. 2. Basis set convergence of the Hartree-Fock binding energy per monomer ΔE_{SCF} in $(\text{HCl})_\infty$. Symbols are chosen as in Fig. 1. The upper and the lower straight lines now refer to the aug-cc-pVXZ and the cc-pVXZ basis sets, in reverse order compared to Fig. 1.

chains as obtained by a least squares fit using Eq. (1) which turns out to describe the Hartree-Fock energies, underlying Figs. 1 and 2, excellently. A three-point fit based on Eq. (1) to the Hartree-Fock energies, obtained with three basis sets X , Y and Z , also yields convincing results that converge rapidly with the quality of the three basis sets used. Halkier et al. [8] found for the basis set convergence of the Hartree-Fock binding energy of several hydrogen-bonded complexes, including $(\text{HF})_2$ and $(\text{HCl})_2$, that the mean of the bare and the counterpoise corrected Hartree-Fock binding energies frequently provides a decent extrapolation to the basis set limit. This behaviour of the mean Hartree-Fock binding energy is solely observed for the aug-cc-pVXZ series for $(\text{HF})_\infty$.

For a systematic treatment of electron correlation in $(\text{HF})_\infty$ and $(\text{HCl})_\infty$, we expand the correlation energy per monomer in terms of Stoll’s incremental scheme [18–20]. This yields a decomposition of the correlation energy per monomer in terms of the correlation energy arising from the electrons of a single monomer within the infinite chains and non-additive contributions from electrons of pairs, triples, ... of monomers. The individual energy increments are obtained using CCSD (as implemented in the MOLPRO program [33,34]) to correlate the valence electrons of selected monomers within the oligomers. The oligomers comprise six to ten monomers and are arranged in the geometry of

Table 1

Basis set extrapolated Hartree-Fock binding energies per monomer $\Delta E_{\text{SCF}}(\infty)$ of $(\text{HF})_\infty$ and $(\text{HCl})_\infty$ obtained by least squares fits to Eq. (1) of their Hartree-Fock energies for the cc-pVXZ ($X = \text{D}, \dots, 6$) and aug-cc-pVXZ ($X = \text{D}, \dots, 5$ for $(\text{HF})_\infty$ and $X = \text{D}, \dots, 6$ for $(\text{HCl})_\infty$) series of basis sets. All data are given in millihartree.

| Compound | BSSE correction | $\Delta E_{\text{SCF}}(\infty)$ | |
|-----------------------|-----------------|---------------------------------|-------------|
| | | cc-pVXZ | aug-cc-pVXZ |
| $(\text{HF})_\infty$ | Non | -10.199 | -10.194 |
| | CP | -10.194 | -10.222 |
| $(\text{HCl})_\infty$ | Non | -0.596 | -0.586 |
| | CP | -0.584 | -0.577 |

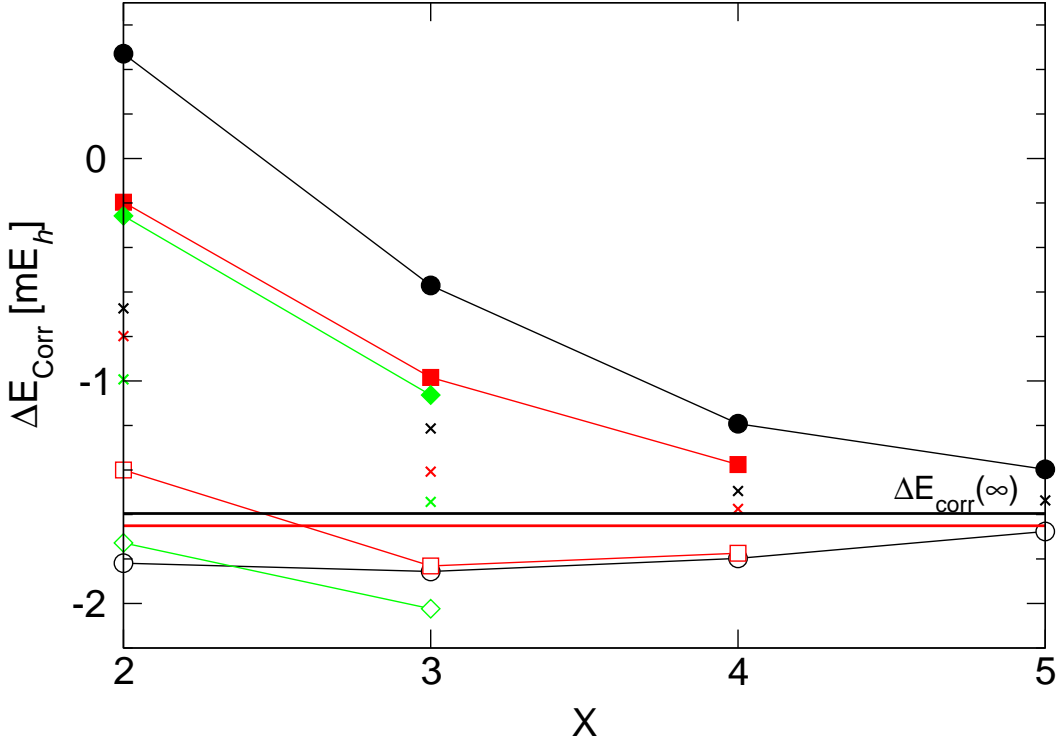


Fig. 3. Basis set convergence of the correlation contribution to the binding energy per monomer ΔE_{corr} in $(\text{HF})_\infty$. Symbols are chosen as in Fig. 1, with diamonds showing data for the d-aug-cc-pVXZ basis sets.

the respective chains, for details see Ref. [16]. BSSE is removed by applying the CP correction [31,32] where only the basis functions of monomers neighbouring the central monomer of those oligomers, used in the calculation of the energy increments, are retained.

The correlation contributions to the binding energies per monomer of $(\text{HF})_\infty$ and $(\text{HCl})_\infty$ are plotted in Figs. 3 and 4. For each series of correlation consistent basis sets, there is an upper curve for the CP corrected binding energies

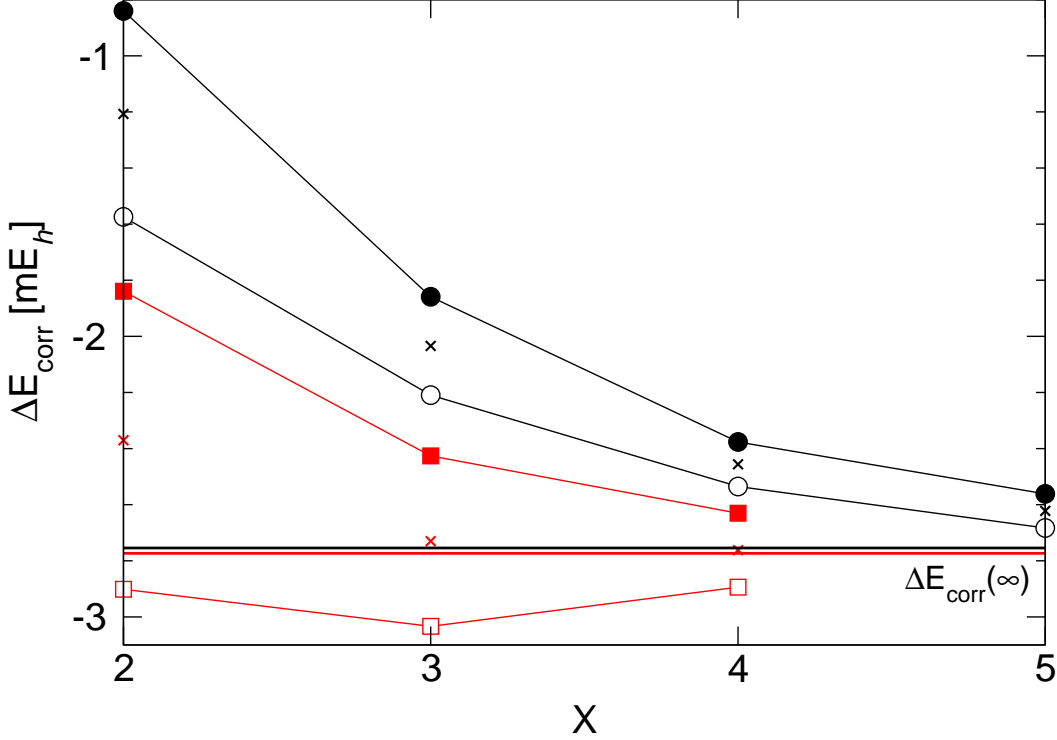


Fig. 4. Basis set convergence of the correlation contribution to the binding energy per monomer ΔE_{corr} in $(\text{HCl})_\infty$. Symbols are chosen as in Fig. 1.

and an lower curve giving the bare binding energies without CP correction of the monomer energies. We note that the CP corrected energies drop monotonically with improving basis set quality but the corresponding bare energies behave unsystematically. The binding energy curves of $(\text{HF})_\infty$ in Fig. 3 for the aug-cc-pVXZ and d-aug-cc-pVXZ basis sets are essentially parallel, if counterpoise correction is applied, but the associated curves for the bare binding energies differ considerably, an effect which is exclusively caused by the behaviour of the monomer energies employed for the bare and CP corrected curves. The small difference between the two CP corrected curves indicates the small improvement of the description of the ground state of a HF monomer and $(\text{HF})_\infty$ by the second set of diffuse functions in d-aug-cc-pVXZ basis sets.

The error of the correlation contribution to the binding energy, introduced by the finite basis sets, can be estimated as the differences of the bare and the CP corrected values corresponding to the same basis set series in Figs. 3 and 4. Using the cc-pV5Z binding energies, the deviation of the bare binding energy from the CP corrected binding energy is $\approx 20\%$ for $(\text{HF})_\infty$ and $\approx 5\%$ for $(\text{HCl})_\infty$, the error being considerably larger for $(\text{HF})_\infty$ compared to $(\text{HCl})_\infty$. The basis set error is far too large for a definitive value of the correlation contribution to the binding energy of the infinite chains.

To get the basis set limit correlation contribution to the binding energies,

Table 2

Basis set extrapolation of the CP corrected correlation contribution to the binding energy per monomer ΔE_{corr} of $(\text{HF})_\infty$ by means of Eqs. (2) and (3). All data are given in millihartree.

| X-Y | $\Delta E_{\text{corr}}(\infty)$ cc-pVXZ | $\Delta E_{\text{corr}}(\infty)$ aug-cc-pVXZ |
|-----------------|---|---|
| X^{-3} D-T | -1.037 | -1.337 |
| D-Q | -1.433 | -1.547 |
| T-Q | -1.637 | -1.655 |
| Q-5 | -1.606 | |
| Park et al. D-T | -1.215 | -1.475 |
| D-Q | -1.496 | -1.593 |
| T-Q | -1.620 | -1.646 |
| Q-5 | -1.585 | |

Table 3

Basis set extrapolation of the CP corrected correlation contribution to the binding energy per monomer ΔE_{corr} of $(\text{HCl})_\infty$ by means of Eqs. (2) and (3). All data are given in millihartree.

| X-Y | $\Delta E_{\text{corr}}(\infty)$ cc-pVXZ | $\Delta E_{\text{corr}}(\infty)$ aug-cc-pVXZ |
|-----------------|---|---|
| X^{-3} D-T | -2.300 | -2.681 |
| D-Q | -2.604 | -2.742 |
| T-Q | -2.760 | -2.773 |
| Q-5 | -2.747 | |
| Park et al. D-T | -2.409 | -2.742 |
| D-Q | -2.642 | -2.764 |
| T-Q | -2.750 | -2.774 |
| Q-5 | -2.762 | |

firstly, we apply a two-point fit based on Eq. (2), involving the correlation energies for the infinite chains, obtained with two basis sets X and Y , and the CP corrected ones for the respective monomers [7]. Secondly, Eq. (3) is harnessed, where the correlation energy of the monomer is required in a very good approximation. As there are no suitable R12 data for HF and HCl, we determine the correlation energy of the monomers by X^{-3} extrapolation (2). For HF, we extrapolate the correlation energies of a cc-pV5Z and a cc-pV6Z calculation, where basis set extension [32], i.e. the basis set improvement due to the basis functions of neighbouring monomers, is accounted for by surrounding the HF monomer by the basis sets of four additional

Table 4

Basis set extrapolated binding energies per monomer $\Delta E(\infty)$ of $(\text{HF})_\infty$ and $(\text{HCl})_\infty$ and their decomposition into basis set extrapolated Hartree-Fock $\Delta E_{\text{SCF}}(\infty)$ and electron correlation $\Delta E_{\text{corr}}(\infty)$ contributions. $\Delta E_{\text{SCF}}(\infty)$ is the mean of the four extrapolated energies for each infinite chain, respectively, in Tab. 1 and $\Delta E_{\text{corr}}(\infty)$ is the mean of the two Q-5 (cc-pVXZ) and the two T-Q (aug-cc-pVXZ) extrapolated energies for each infinite chain, respectively, in Tabs. 2 and 3. All data are given in electronvolt.

| | $(\text{HF})_\infty$ | $(\text{HCl})_\infty$ |
|----------------------------------|----------------------|-----------------------|
| $\Delta E_{\text{SCF}}(\infty)$ | -0.2776 | -0.01594 |
| $\Delta E_{\text{corr}}(\infty)$ | -0.0442 | -0.07521 |
| $\Delta E(\infty)$ | -0.3218 | -0.09115 |

monomers which yields $E_{\text{corr, HF}} = -0.314530 E_h$. For the HCl monomer, the basis sets of only two neighbouring HCl monomers is utilised in the extrapolation of aug-cc-pV5Z and aug-cc-pV6Z correlation energies, yielding $E_{\text{corr, HCl}} = -0.254373 E_h$.

Two-point extrapolations for $(\text{HF})_\infty$ and $(\text{HCl})_\infty$ are displayed in Tabs. 2 and 3, and are found to converge rapidly towards a limit with increasing quality of the involved basis sets. The most reliable extrapolations to the limit are obtained, if basis sets of largest X and $X + 1$ are employed. For several molecules, this fit was shown to yield the best approximation to the basis set limit, with respect to accurate R12 data, for the correlation contribution to the binding energy [7]. The extrapolations obtained with cc-pVXZ and aug-cc-pVXZ series are found to approach each other as they should. Inspecting Figs. 3 and 4, we observe that the extrapolations involving the best basis sets, i.e. with largest X and $X + 1$, lie well in the range where they are expected to be, leading to the conclusion that the basis set limit is nearly reached. The very good agreement of the best extrapolated values [Q-5 for cc-pVXZ and T-Q for aug-cc-pVXZ] indicates reliability for the correlation contribution to the binding energies of both chains. Especially X^{-3} extrapolations involving double ζ quality basis sets in Tabs. 2 and 3 are found to be less accurate than corresponding extrapolations by Park et al. with respect to the values of Q-5 extrapolation [cc-pVXZ] or the ones of T-Q extrapolation [aug-cc-pVXZ], as the latter extrapolation method is independent of the convergence properties of the series [4, 6] underlying X^{-3} extrapolation (2). The mean of corresponding bare and CP corrected energies [8] does only provide a decent approximation to the basis set limit binding energies for $(\text{HF})_\infty$ [Fig. 3], the results for $(\text{HCl})_\infty$ are contradictory [Fig. 4].

4 Conclusion

In our study we focus on the basis set convergence of the Hartree-Fock and the correlation energy in the *infinite* chains $(\text{HF})_\infty$ and $(\text{HCl})_\infty$. Especially in hydrogen bonded systems, the binding energy per monomer is very small and very accurate calculations are required. Our data shows that the error of the binding energy, employing the cc-pV5Z basis set, leads to a deviation of the bare binding energy per monomer of $(\text{HF})_\infty$ from the CP corrected one by $\approx 20\%$ and by $\approx 5\%$ for $(\text{HCl})_\infty$ which is too large to be satisfactory.

To reduce the error, we extrapolate Hartree-Fock [3] and correlation energies [5–10] where two different extrapolation schemes are studied for the correlation energy. The accuracy of the resulting correlation contribution to the binding energies in Tab. 4 is estimated by the deviation of the extrapolated binding energies for the aug-cc-pVXZ series from the ones for the cc-pVXZ series, where the largest basis sets of the respective series [T–Q for aug-cc-pVXZ and Q–5 for cc-pVXZ] are utilised as they could be shown to yield the best results. The deviation is $\approx 3\%$ or $\approx 4\%$ for $(\text{HF})_\infty$ and $\approx 1\%$ or $\approx 0.4\%$ for $(\text{HCl})_\infty$ depending on the extrapolation method employed, i.e. X^{-3} [5–8] or Park et al. [9, 10].

We would like to point out further, that Eqs. (2) and (3) facilitate to extrapolate the individual energy increments occurring in the decomposition of the correlation energy in terms of the incremental scheme [16, 18–20], separately. This is advantageous for treating, e.g., hydrogen bonds in larger molecules and facilitates a more accurate treatment of different atoms or fragments in crystals.

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